

## The Structure of Epoxy Resins Using NMR and GPC Techniques

M. G. ROGERS, *Research Department, Dow Chemical of Canada, Limited,  
Sarnia, Ontario, Canada*

### Synopsis

A series of epoxy resins based on the diglycidyl ethers of bisphenol A have been characterized by nuclear magnetic resonance and gel permeation chromatography. The ratio of molecular volume of a lightly branched molecule to that of a linear molecule of the same weight was found to vary as the square root of the ratio of the average maximal dimensions of the chain. At high degrees of chain branching, the ratio of the latter was to the power of three halves.

### INTRODUCTION

Numerous chemical and instrumental techniques have been described for the analysis of epichlorohydrin-bisphenol A polymers.<sup>1</sup> Very little information exists in the literature on the use of gel permeation chromatography<sup>2,3</sup> and nuclear magnetic resonance<sup>1</sup> for the characterization of these polymers. Recently, we described a method for determining the amount of chain branching in epoxy resins.<sup>4</sup> The current report shows how, combined with GPC data, information obtained by NMR can be utilized for determining the structure of epoxy resins.

### EXPERIMENTAL

A Waters Associates Model 200 gel permeation chromatograph was used to determine the molecular size of the samples. The instrument was fitted with five columns of nominal permeability limits of  $10^6$ ,  $10^5$ ,  $10^4$ ,  $10^3$ , and  $10^2$  Å. The eluting solvent was trichlorobenzene at 135°C. The average weight of sample injected, as a 0.75% w/w solution, was 7.5 mg. The instrument was calibrated with low molecular weight, anionic polymerized polystyrenes of known molecular size, together with a series of well-characterized polyethylene glycols and one sample each of high-purity, monomeric diglycidyl ether of bisphenol A, ethylbenzene, bisphenol A, *p*-xylene, decane, and methanol. A calibration curve was constructed by plotting molecular size, measured as "effective carbon number," versus elution volume. The "effective carbon number" was calculated according to the rules set out by Hendrickson and Moore.<sup>5</sup>

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TABLE I  
Polymer Characteristics Determined by NMR and GPC

Sample no.	<i>EEW</i>	<i>m</i> <sup>a</sup>	Molecular size, <sup>b</sup> #C units	Molecular weight distribution $\bar{M}_w/\bar{M}_n$ <sup>b</sup>
1	547	0	65	1.6
2	979	0	94	1.6
3	1378	0	114	1.9
4	1829	0	142	1.6
5	2654	0	186	1.9
6	176	0	15	1.1
7	189	0	17	1.3
8	3257	0	220	1.7
9	300	0	40	1.3
10	1740	0	135	1.5
11	811	0.7	73	1.4
12	1009	0.3	90	2.0
13	1235	1.5	92	1.7
14	1291	0.35	106	1.7
15	1291	0.8	104	1.8
16	1134	1.2	88	1.7
17	1240	0.62	104	1.7
18	2530	1.5	182	1.6
19	2324	1.95	145	2.5
20	1520	1.95	104	1.8

<sup>a</sup> Determined by NMR.

<sup>b</sup> Determined by GPC.

The number of repeat units in the polymer chain was calculated from eq. (1):

$$n = \frac{2(EEW - 170)}{284} \quad (1)$$

where *EEW* is defined as the epoxy equivalent weight<sup>1</sup> of the resin; 170 is the *EEW* with *n* = 0.

The average number of branch points in the samples was determined using a Varian A-60 NMR spectrometer. Details of the procedure are given elsewhere.<sup>4</sup> Briefly, the method involves reacting trichloroacetyl isocyanate with the hydroxyls present in the epoxy resin to form a urethane structure. This produces a downfield shift of the associated methine proton absorption in the nuclear magnetic resonance spectra and allows the relative number of protons in each position to be calculated. Peak area comparisons, combined with considerations of model structures, gives a means of calculating the number of chain branches in the sample.

The results are presented in Table I for both linear and branched polymers.

## RESULTS AND DISCUSSION

The molecular dimension of a linear polymer is frequently expressed as the root-mean-square radius of gyration  $(\bar{R}^2)^{1/2}$  or end-to-end distance  $(\bar{h}^2)^{1/2}$ . Coll and Gilding<sup>6</sup> concluded that, in the case of linear molecules,  $(\bar{R}^2)^{1/2}$  or  $(\bar{h}^2)^{1/2}$  are universal parameters that determine the elution volume in GPC.

The end-to-end distance of a polymer with  $n$  freely rotating segments, each of effective length  $b$ , is given by

$$\bar{h}^2 = nb^2.$$

The molecular size can be calculated from a determination of the number of segments and a knowledge of the length of each segment of the molecule. The latter may be determined from Godfrey molecular models<sup>19</sup> and a theoretical molecular size calculated. These calculations were performed for the present results, and it was found that the experimentally determined molecular size was smaller than that predicted, indicating that the molecules are quite coiled. If one considers that one of the controlling factors in GPC separation is the maximum polymer size that can penetrate a gel pore, one should calculate an average maximal cross-sectional dimension of the coil. Kuhn<sup>20</sup> has shown this to be  $0.7(\bar{h}^2)^{1/2}$ . The experimental and calculated values then coincide. The referee has pointed out that the mole-

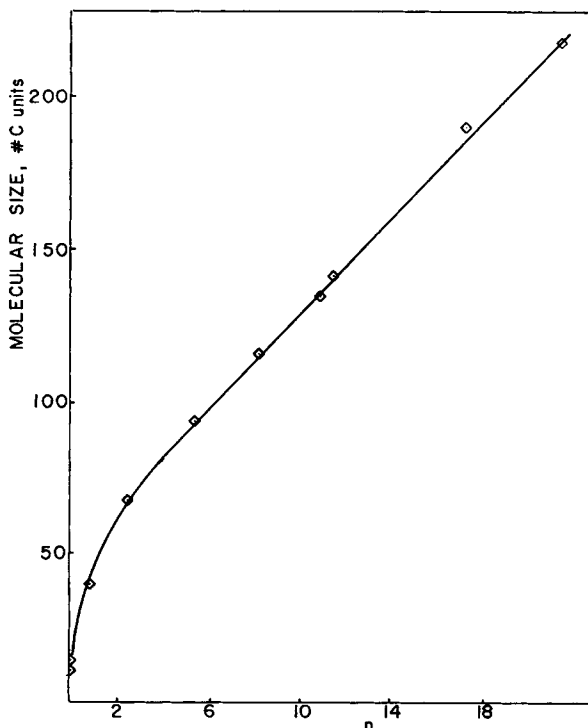


Fig. 1. Average molecular size vs. number of repeat units for linear polymers.

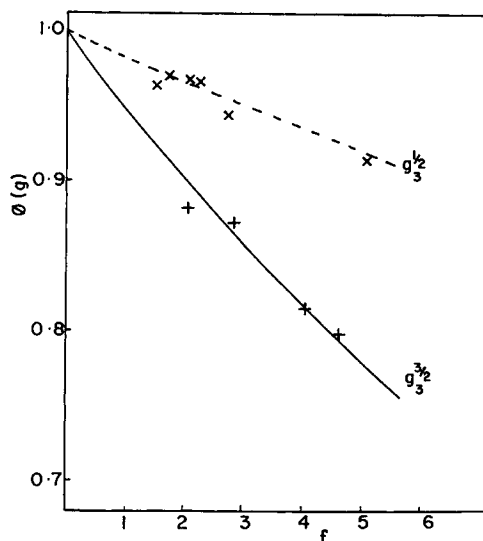


Fig. 2. Plot of  $\phi(g)$  [ $= g^{1/2}$  or  $g^{3/2}$ ] as a function of the number of branches in the molecule: (X) lightly branched; (+) highly branched.

cules contain a few segments only and it is unlikely that this approach is valid. However, Stockmayer and Fixman<sup>21</sup> have indicated that even if the chains constituting the polymer molecule do not follow random-flight statistics, the same equations may be used. In view of our ability to now measure branching, this requires further experimentation.

An alternative procedure involves the use of "effective carbon number" and has previously been applied to epoxy resins by Larsen<sup>7</sup> and Biesenberger et al.<sup>8</sup>

The average sizes, as determined by GPC, of the linear diglycidyl ethers of bisphenol A are plotted as a function of the number of repeat units,  $n$ , in Figure 1. Initially, the size of the molecule increases rapidly with increasing number of repeat units until approximately  $n = 2$ . Thereafter, the size increases linearly with increasing number of repeat units to give a straight line of constant slope 7.7 carbon atom chain length (#C) per repeat unit. This compares with a calculated value of 13.7 #C and the 9.0 #C found by Larsen for epoxy resins in tetrahydrofuran.

In the case of branched molecules, Hendrickson and Moore<sup>5</sup> and Hendrickson<sup>9</sup> found that structural elements are additive in their effect, and one may again calculate a molecular size based on the "effective carbon number." Assuming that this assumption is valid for epoxy resins, then one might expect the ratio of (#C branched)/(#C linear) for molecules of the same chemical structure and molecular weight to depend on the number of functional branch points. Again, since the "effective carbon number" is a measure of molecular size, which in turn is related to the intrinsic viscosity  $[\eta]$  of the solution, the ratio (#C branched)/(#C linear) should vary according to  $([\eta] \text{ branched})/([\eta] \text{ linear})$ . Thurmond and Zimm<sup>10</sup> found

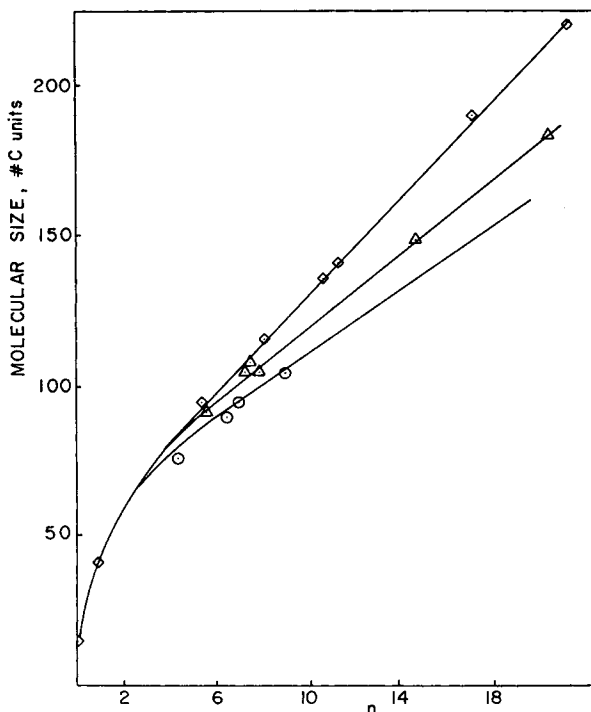


Fig. 3. Average molecular size vs. number of repeat units: ( $\square$ ) linear polymer; ( $\Delta$ ) lightly branched polymers,  $0 < f < 1/2n$ ; ( $\odot$ ) highly branched polymers,  $1/2n < f < n$ .

that the latter ratio varied as  $g_x^{3/2}$ , where  $g_x$  is the ratio of the mean square radii of branched and linear molecules. Other authors have found that  $g_x^{3/2}$  overestimates the effect of branching and have suggested  $g_x^{1/2}$  as an alternative.

In the case of a fractionated polymer, which originally was polydispersed, it is possible to calculate the average value of  $g_x$  for a given fraction as a function of the mean number of branching points  $m$  present per molecule. For trifunctional branching, Zimm and Stockmayer<sup>11</sup> have found

$$g_3(m) = \left[ (1 + m/7)^{1/2} + \frac{4m}{9\pi} \right]^{-1/2}. \quad (2)$$

Figure 2 shows a plot of  $g_3^{1/2}(f)$  and  $g_3^{3/2}(f)$  as a function of the average number of branches  $f (=2m + 1)$  in the molecule. The curves were calculated from eq. (2). The experimental points are the ratio of the molecular size, as determined by GPC, of the branched molecule to that of the linear molecule of the same epoxy equivalent weight. The *EEW* is proportional to molecular weight.<sup>1</sup> At low degrees of branching,  $g^{1/2}$  is the preferred function, while at high degrees of branching,  $g^{3/2}$  fits the experimental results. For the purposes of the current investigation, the polymer is regarded as having a low degree of branching when  $f < n/2$ .

In other polymer systems, it has been assumed that  $g^{1/2}$  exaggerates the effect of structure on viscosity. However, on closer examination of the literature data, it is seen that a low degree of branching favors the  $g^{1/2}$  rule<sup>12-15</sup>; but when a significant number of branches is present, the  $g^{3/2}$  rule is followed.<sup>16-18</sup>

Bearing in mind that the reproducibility of GPC measurements is  $\pm 5\%$ , and taking the arbitrary definition for low and high degrees of branching, theoretical molecular size curves as a function of the number of repeat units in the molecule can be constructed (Fig. 3). The fit of the experimental results is very good.

Throughout this investigation, only average values of molecular size and branching have been determined. It would be interesting to examine the degree of branching within each polymer fraction, the effects of increasing molecular size distribution, and the effect of changing the solvent system.

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